

Short communication

Synthesis of carbon-coated Li_3VO_4 and its high electrochemical performance as anode material for lithium-ion batteries



Zhiyong Liang^a, Yanming Zhao^{b,c,*}, Liuzhang Ouyang^a, Youzhong Dong^a, Quan Kuang^a, Xinghao Lin^a, Xudong Liu^a, Danlin Yan^a

^a School of Material Science and Engineering, South China University of Technology, China

^b School of Physics, South China University of Technology, Guangzhou 510640, China

^c Key Laboratory of Clean Energy Materials of Guangdong Higher Education Institute, China

HIGHLIGHTS

- Carbon-coated Li_3VO_4 composite is firstly synthesized by simple sol–gel method.
- Residual carbon and reducing atmosphere would not change the valence of V (+5).
- The carbon-coated Li_3VO_4 shows a reversible capacity of $\sim 480 \text{ mAh g}^{-1}$ at 0.18C.
- The carbon-coated Li_3VO_4 presents outstanding rate abilities and cycle capabilities.

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ABSTRACT

Carbon-coated Li_3VO_4 sample is synthesized by a simple sol–gel method. X-ray diffraction and X-ray photoelectron spectroscopy results show that single-phase Li_3VO_4 can be obtained in a reducing atmosphere with the valence of vanadium of +5. The final product sintered at 650 °C demonstrates a favorable electronic conductivity with 6.12% residual carbon. Electrochemical testing shows that the carbon-coated Li_3VO_4 sample display a discharge capacity of 662.6 mAh g^{-1} and 507.4 mAh g^{-1} at 0.18C in the first and the second cycle, respectively, and a reversible capacity (charge capacity) of $\sim 480.0 \text{ mAh g}^{-1}$ can be obtained in the second cycle. Furthermore, the discharge–charge capacity of the sample can retain $\sim 180 \text{ mAh g}^{-1}$ and $\sim 90 \text{ mAh g}^{-1}$ at 12C and 40C, respectively.

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1. Introduction

Lithium-ion batteries (LIBs) are regarded as the most promising energy storage devices for portable electronics and hybrid electric vehicles (HEVs). One of the key safety issues in LIBs for HEVs is dendritic lithium growth on the anode surface at high charge current because of that conventional graphite materials approach almost 0 V versus Li^+/Li at the end of Li insertion [1]. Therefore, extensive attention has been paid to the development of new anode materials [2,3]. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with the spinel structure is identified as a promising anode material due to its good reversibility and nearly inconsiderable volume changes during the intercalation process.

However, the Li insertion potential of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is relatively high (~1.5 V) in comparison with that of ~0.1 V for graphite. This significantly reduces the overall cell voltage and cancels out the benefits of using a dense oxide as cathode material. Although recent reports revealed that Li^+ can be reversibly intercalated into the layered $\text{Li}_{1+x}\text{V}_{1-x}\text{O}_2$ at a potential of ~0.1 V versus Li^+/Li , problems of fast deterioration of this material remain unresolved [4–7].

Recently, another lithium transition metal oxide, Li_3VO_4 , has been reported to be a promising lithium intercalation host with both lower average discharge–charge potential (0.5–1.5 V) than that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and relatively good cycle capability during discharge–charge process [8,9]. However, Li_3VO_4 suffers from low electronic conductivity, which may cause poor electrochemical performance and limit its practical application.

Here carbon-coated Li_3VO_4 was carried out for the first time via a simple sol–gel method. Surprisingly, the structure and valence of

* Corresponding author. School of Physics, South China University of Technology, Guangzhou 510640, China. Tel.: +86 20 87111963; fax: +86 20 85511266.

E-mail address: zhaoym@scut.edu.cn (Y. Zhao).

vanadium (+5) of Li_3VO_4 remain unchanged even in the presence of carbon and reducing atmosphere. The carbon-coated Li_3VO_4 sample has been tested as anode material for lithium ion battery, and it exhibited a very high reversible capacity and good rate ability.

2. Experimental

The carbon-coated Li_3VO_4 sample was synthesized by a simple sol-gel method where citric acid was used as both chelating agent and carbon source. First of all, stoichiometric amounts of V_2O_5 (0.919 g) and $\text{LiCH}_3\text{COO} \cdot 2\text{H}_2\text{O}$ (3.092 g) were added in 80 mL distilled water under magnetic stirring at 60 °C for 0.5 h. Secondly, citric acid (2.112 g) with a molar ratio of citric acid: vanadium = 1:1 was added to the obtained orange solution. Then the solution was heated at 80 °C under constant stirring to remove the excess water till the solution became a gel. After drying in an oven at 80 °C for 48 h, the gel was preheated at 350 °C for 4 h under a stream of reducing atmosphere (30% H_2 + 70%Ar). Finally, the precursor mixtures were reground and sintered at various temperatures (550 °C, 600 °C, 650 °C and 700 °C) for 6 h under the same ambience. For comparison, carbon-free Li_3VO_4 was also prepared by sintering the precursor mixtures at 650 °C for 6 h under air ambience.

The resulting samples were characterized by X-ray diffraction (XRD) with monochromited Cu K α radiation. The carbon content was verified by Vario EL CHNS elemental analyzer. X-ray photo-electron spectroscopy (XPS) was obtained for the sample (sintering at 650 °C) using a Kratos Axis Ultra spectrometer. The electronic conductivity was measured according to linear four-point probe method by using an RTS-8 measurement system. The morphology of the synthesized samples was examined by a scanning electron microscopy (SEM, Hitachi S4800) and the microstructure of the samples was observed by a high resolution transmission electron microscopy (HRTEM, Hitachi 7650) operating at 300 kV.

The electrochemical properties of carbon-coated Li_3VO_4 samples as anode were evaluated with two-electrode electrochemical cell by an automatic battery tester system (Land®, China). The anode film was prepared by mixing the as-synthesis sample with acetylene black and polyvinylidene fluoride (PVDF) binder in a weight ratio of 8:1:1 in N-methyl-2-pyrrolidone (NMP). The obtained slurry was coated on Cu foil uniformly. Two-electrode electrochemical cells were assembled in a Mikrouna glove box filled with ultra-high argon. Lithium metal foils were used as counter electrodes, Celgard® 2320 as separator, and 1 M LiPF_6 in EC: DMC (1:1 vol. %) was used as electrolyte. Cyclic voltammetry (CV) were performed with an AUTOLAB PGSTAT302N (Metrohm, Netherlands) in 0.1–2.5 V at a scanning rate of 0.1 mV s⁻¹.

3. Results and discussion

The XRD patterns of carbon-coated Li_3VO_4 obtained at various temperatures are shown in Fig. 1. For the sample sintered at 550 °C, a small amount of Li_2CO_3 phase is detected in addition to the dominated orthorhombic Li_3VO_4 phase, while for the samples sintered at 600 °C, 650 °C and 700 °C, all the diffraction peaks can be indexed as a single phase by Dicvol program. The diffraction intensity becomes stronger along with the increasing temperature, indicating a better crystallinity of the sample. The indexing results of $a = 5.435(8)$ Å, $b = 6.322(1)$ Å and $c = 4.942(8)$ Å in orthorhombic system agree well with that of β polymorph Li_3VO_4 phase (JCPDS No. 38-1247). The contents of residual carbon measured by element analysis are 7.05%, 6.12%, and 5.34% in the final product of the samples sintered at 600 °C, 650 °C and 700 °C, respectively. And the carbon should be amorphous since no peaks attributed to crystalline carbon can be detected in the XRD patterns. The linear

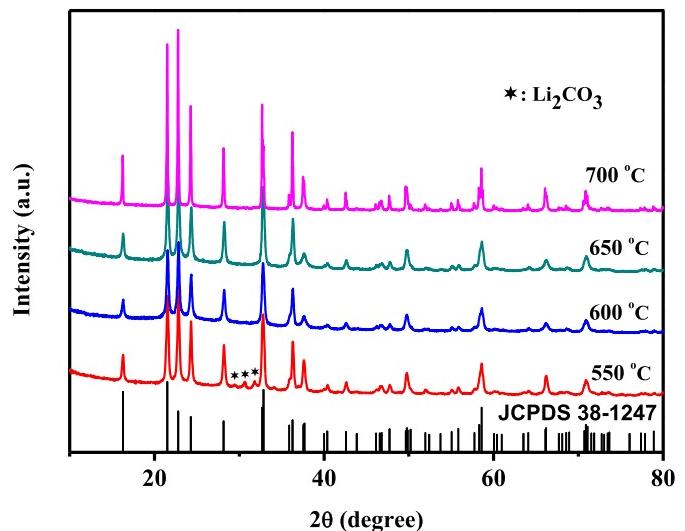


Fig. 1. XRD patterns of standard Li_3VO_4 (JCPDS No. 38-1247) and the samples synthesized at various temperatures.

four-point probe measurement results (sample sintered at 650 °C) show that its electronic conductivity is 4.76×10^{-3} S cm⁻¹, which is 2 orders of magnitude higher than that of carbon-free Li_3VO_4 (measure at 500 K) [10].

Fig. 2(a) shows the experimental values of the X-ray photo-electron spectroscopy (XPS) for V 2P in the sample (sintered at 650 °C). A binding energy (BE) of 517.7 eV observed here matches well with previous report for pure Li_3VO_4 (517.5 eV) [11]. This result indicates that the valence of vanadium in the carbon-coated Li_3VO_4 sample is +5. Combined with the XRD and XPS results, we conclude that the existence of residual carbon and reducing atmosphere would not change the structure of Li_3VO_4 as well as the valence of vanadium (+5).

Representative microstructures of the carbon-coated Li_3VO_4 sample sintered at different temperatures are compared in Fig. 2(b–d). For the sample sintered at 600 °C, the particles with the particle size less than 80 nm which are agglomerated together can be observed in Fig. 2(b), while for the sample sintered at 700 °C (shown in Fig. 2(d)) non-uniform particles (larger than 120 nm) can be seen. On the contrary, the sample sintered at 650 °C has better dispersion and narrower particles size distribution of ~100 nm (shown in Fig. 2(c)), which agree well with the TEM image shown in Fig. 2(e). As depicted in the HRTEM image (Fig. 2(f)), the crystalline region with clear lattice fringes has an inter-planar spacing about 0.272 nm, which can be index to (2 0 0) atomic plane of the orthorhombic Li_3VO_4 . Furthermore, an amorphous carbon layer with thickness about 3.2 nm can be observed coating on the particles, which is in accordance with the XRD and elemental analysis results. It is believed that this carbon layer makes great contribution to the restriction of grain growth and increasing electronic conductivity, which is significant for improving the electrochemical performance of the electrode.

Fig. 3(a) shows the representative capacity–voltage curves of carbon-coated Li_3VO_4 sample (sintered at 650 °C) in 0.1–2.5 V. The electrochemical profiles at low rate are well consistent with previously reported results [8,9]. The carbon-coated Li_3VO_4 sample display a discharge capacity of 662.6 mAh g⁻¹ and a charge capacity of 475.1 mAh g⁻¹ at 0.18C (1C = 500 mA g⁻¹) with an initial coulombic efficiency of 71.7% in the first cycle and a reversible capacity of ~480.0 mAh g⁻¹ can be obtained in the second cycle. The relatively low initial coulombic efficiency may be attributed to the irreversible capacity lost, including side reactions such as formation

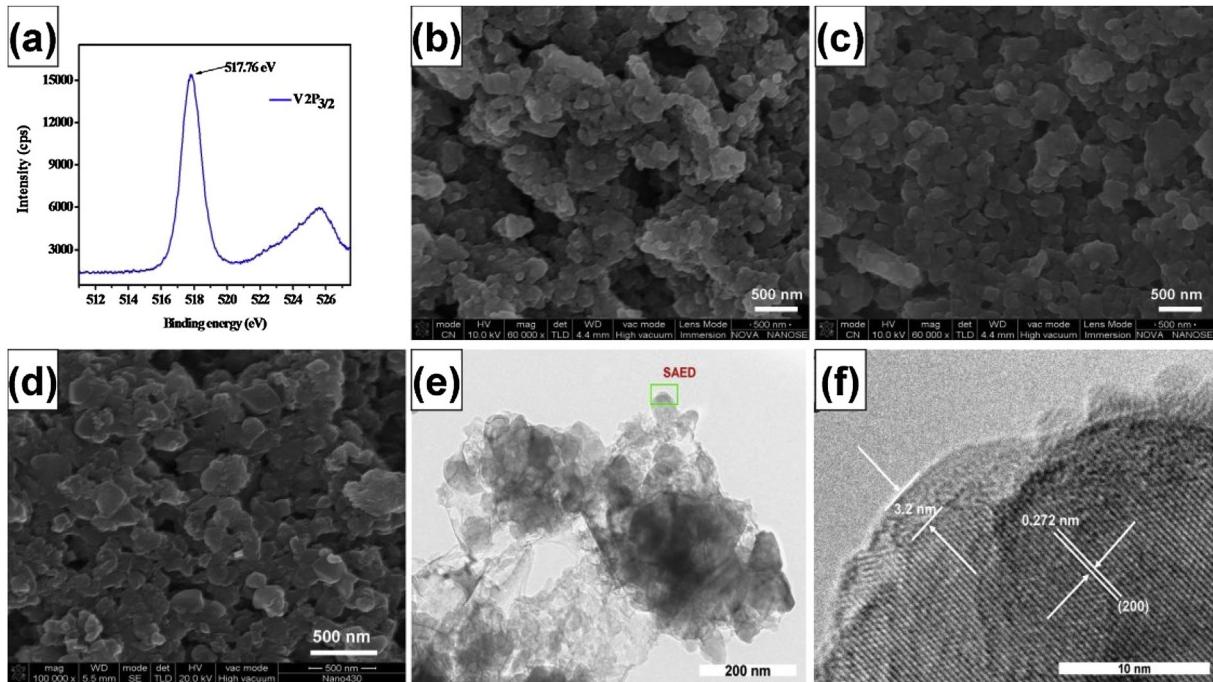


Fig. 2. Characterization of as-synthesis carbon-coated Li_3VO_4 sample: (a) X-ray photoelectron spectroscopy of V 2P; (b–d) SEM images of samples synthesized at various temperatures; (c) TEM image and (d) HRTEM image of sample sintered at 650 °C.

of solid electrolyte interface (SEI) film and decomposition of electrolyte [5,8]. As shown in Fig. 3(a), the capacities of the carbon-coated Li_3VO_4 decrease along with the increasing of current rates and, even at a high current rate of 40C, the capacities can still retain about 95 mAh g⁻¹. The CV curves of carbon-coated Li_3VO_4 sample are shown in Fig. 3(b). As it can be seen, the CV curve of the first cycle shows three reduction peaks (about 0.55 V, 0.45 V and 0.35 V)

which indicates three phase transformations during lithium insertion, while for the CV curves of the second and the third cycles, only two reduction peaks (about 0.83 V and 0.47 V) can be observed. These changes are usually ascribed to the occurrence of side reactions on the electrode surfaces and interfaces due to the SEI formation as well as phase transformations, which is similar to Fe_3O_4 anode material [12]. The oxidation peaks observed in CV

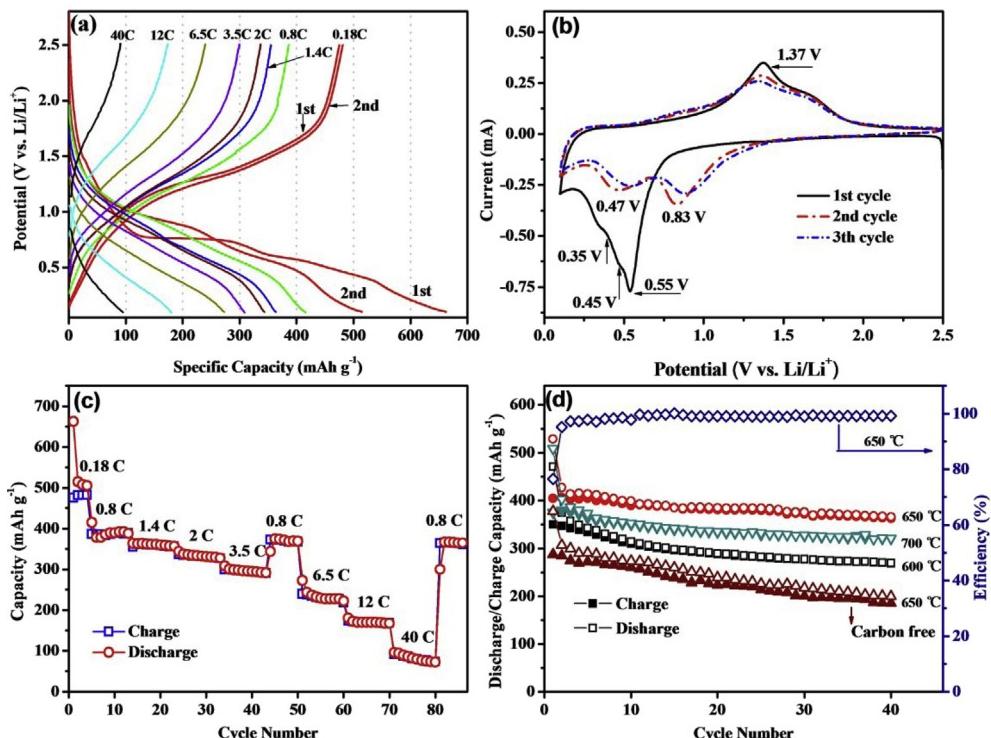


Fig. 3. (a) Discharge–charge curves, (b) CV curves, (c) rate abilities and (d) cycling stability of Li_3VO_4 sample in the voltage of 0.1–2.5 V.

curve of the 1st–3rd cycle remain fairly consistent (about 1.37 V), indicating a similar lithium extraction process.

Fig. 3(c) shows the rate abilities of carbon-coated Li_3VO_4 at different discharge–charge rates, and finally in 0.8C succession. As shown in **Fig. 3(c)**, the carbon-coated Li_3VO_4 sample has a reversible capacity (charge capacity) of $\sim 480 \text{ mAh g}^{-1}$ at 0.18C in the 1st–4th cycle. Further more, it can export more than 300 mAh g^{-1} at 3.5C rate, namely >50% of the theoretical capacity can be achieved within 20 min. The discharge–charge capacity can retain $\sim 180 \text{ mAh g}^{-1}$ and $\sim 90 \text{ mAh g}^{-1}$ at the rate of 12C and 40C, respectively. It should be emphasized that discharge capacities of 374.7 mAh g^{-1} and 366.9 mAh g^{-1} at 0.8C can be recovered even after discharge–charge at 3.5C and 40C, respectively, which are close to the limit capacity (372 mAh g^{-1}) of the graphite anode. For comparison, cycling stabilities of samples sintered at different temperatures are presented in **Fig. 3(d)**. The sample heated at 650°C shows both higher capacity and better cycling stabilities than others. After 40 cycles at 0.8C, the discharge capacity and charge capacity can retain 365.9 mAh g^{-1} and 363 mAh g^{-1} , respectively, which are 85.9% and 89.8% of the value obtained in the second cycle. Also, cycling stabilities of carbon-free Li_3VO_4 is showed in **Fig. 3(d)**, which indicates both poorer cycle performance (the capacity of 40th cycle is $\sim 65\%$ of the second cycle) and lower discharge–charge capacities when compared to carbon-coated samples. The coulombic efficiencies of sample heated at 650°C are also shown in **Fig. 3(d)**. All coulombic efficiencies can retain almost 100% except for the first few cycles. As for the samples of 600°C and 700°C , only a capacity of $\sim 340 \text{ mAh g}^{-1}$ and $\sim 270 \text{ mAh g}^{-1}$ can be obtained, respectively, which are 72% and 79% of the value of second cycle. These results are consistent with the SEM results (**Fig. 2(b–d)**). Our results confirm that the incorporation of amorphous carbon by sol–gel method, which is significant for improving conductivity and particle size reduction, can greatly improve the electrochemical performance of Li_3VO_4 .

4. Conclusions

Carbon-coated Li_3VO_4 sample has been synthesized by sol–gel method. Our experimental results showed that the carbon-coated

Li_3VO_4 sample has excellent structure stability. Although the valence of vanadium is +5, it can be easily synthesized even in the presence of carbon and reducing atmosphere. The final product of sample sintered at 650°C demonstrates a favorable electronic conductivity with 6.12% residual carbon. The carbon-coated Li_3VO_4 presents a discharge capacity of 662.6 mAh g^{-1} and a charge capacity of 475.1 mAh g^{-1} at 0.18C in the first cycle and a reversible capacity of $\sim 480.0 \text{ mAh g}^{-1}$ can be obtained in the second cycle. The sample sintered at 650°C shows both higher capacity and better cycling stabilities than others. Furthermore, the sample also shows excellent rate ability with the discharge–charge capacity of $\sim 180 \text{ mAh g}^{-1}$ and $\sim 90 \text{ mAh g}^{-1}$ at 12C and 40C, respectively. Further investigations about mechanism and improvement of this material still need to be done in the next work.

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